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A method of metallizing the surface of a solid polymer substrate and the product obtained

- 5 The present invention relates to a method of metallizing the surface of polymer substrates such as polyolefins, fluorine containing polymers, polyalkylenes, polyarylenes and mixtures thereof and the product obtained.
- 10 Polymer surfaces with low surface energy such as untreated or unmodified polymer substrates are in general difficult to metallize using conventional methods based on electroless or galvanic plating methods.
- 15 One approach to obtain metallization on polymer surfaces is given in US 3,801,368, based on the fact that an electroless plating from a solution can be carried out, provided that the surface is first doped using noble metals like Au or Pt. The doping of the surface with noble met-
- 20 als prior to plating is, according to US 3,801,368, carried out by a vacuum evaporation or sputtering process. The advantage of using this type of process is that the energy of the metal-atoms hitting the surface often is sufficient to ensure a good bonding between the subse-
- 25 quently plated metal-film and the polymer surface.

The method described in US 3,801,368 is not universally applicable, but limited to certain polymers. Prior to the doping of the surface by noble metals, it is thus often

30 necessary to modify the chemical composition of the surface, in order to obtain sufficient adhesion between the subsequently plated film and the polymer surface.

The required change of chemical composition, or surface

35 treatment, depends on the substrate to be treated. Corona treatment is widely employed. The corona discharge con-

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sists of a number of small sparks created between the substrate surface and a counter electrode (a silent discharge). Most often this treatment is carried out in ambient atmosphere, and results in erosion of the surface as well as in a generation of free radicals due the energy density of the discharges and the reactivity of the atmosphere. One of the problems regarding this method is, that it is not suited for treatment prior to metallizing strongly curved surfaces or surfaces with many cavities. Other problems relate to the limited control over the resulting chemical composition of the surface.

Often a simple corona treatment is not sufficient and more specialised methods <sup>have</sup> ~~has~~ to be employed to ensure a sufficient adhesion.

One possible method is described in WO 97/37844, where a method to obtain a coupling layer between the surface to be plated and the plated metal-film is described. According to WO 97/37844, the coupling layer is formed by vacuum deposition of a monomer on the surface, which is subsequently polymerised by an irradiation process. To ensure a good coupling between the surface and the coupling layer, and between the coupling layer and the plated metal film, plasma-treatment can be used. This process is especially suited for treatment of polymer films of infinite lengths, as the different processes (plasma-treatment, deposition of coupling layer and polymerisation of coupling layer) are carried out at different, separate, stations.

The nature of this process makes it furthermore not suitable for treatment of fluorine containing polymers like poly-tetra-fluoro-ethylene (PTFE).

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fluoro

A number of patents describe methods for electroless plating of PTFE. In JP 92-240189 a PTFE substrate is irradiated with UV laser in the presence of amine or amide followed by an immersing in an electroless metal plating bath. This results in a good bonding of the plated metal to the substrate. However, this method is very difficult to control and also very expensive.

US 3,956,535 discloses a further method of metallization where the object to be metallized is coated with a film having incorporated therein a hydrolysed metal complex. Upon this metal complex a metal or metal ion is adsorbed and acts as catalyst for autocatalytic metal deposition. This method is not usable on many types of polymer substrates due to poor adhesion between the coated film and the substrate.

Also US 4,952,286 describes a method which includes immersing an article to be plated into an electrolytic bath containing dissolved plating metal. Before immersing, the surface has been provided with areas of catalytic metal chalcogenide coating to be converted to a chemical resistant metal-coating.

US 4,057,663 describes a method to make hydrophobic polymers suitable for electroless plating using a concentrate containing  $P_2O_5$ . This method is particularly suitable for polymers containing fluor, but not very useful for other polymers.

US 4,919,768 discloses another expensive method of metallization, where non-conducting surfaces are provided with a metal sulphide coating, acting as a base for direct electroplating.

Common to the above mentioned methods are, that they are either very expensive, complicated to use or not applicable to various types of polymer substrates.

- 5 The object of the present invention is to provide an industrially applicable method of binding a metal layer to a polymer substrate, which method does not comprise the above mentioned problems, resulting in good binding strength, and can be used on most polymer substrates.

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Another object of the present invention is to provide a fast method of binding a metal layer to a polymer surface, and thereby provide a good binding strength.

- 15 A further object of the present invention is to provide a method of metallizing a polymer surface, which does not result in any severe depolymerisation of the polymer substrate, in particular when the substrate material exhibits fluorine and/or tertiary carbon atoms, and by use of which method the surface affinity against the metal is improved.

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A further object of the present invention is to provide a metallized polymer surface, which can be enhanced by electrochemical deposition using any conventional method.

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Another object of the present invention is to provide a method for metallizing a polymer substrate, which method is economical acceptable.

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A further object of the present invention is to provide a method for metallizing a polymer substrate, which method is uncomplicated to use.

*9 of an injection moulded polymer component*

These objects are achieved by a method of metallizing a surface of a solid polymer substrate<sup>9</sup> comprising the steps of

- 5 a) generating radicals on the substrate surface by subjecting it to a gas plasma,
- b) forming a layer on the surface using a plasma enhanced polymerisation process employing one or more monomers comprising monomers selected among cyano acrylate, mono-  
10 and diacrylates, such as acrylic acid, triethylen glycol diacrylat, glycidyl acrylat, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl  
15 methacrylat, allylic and vinylic compounds, such as vinyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl-alcohol, allyloxymethylsilane, allylphenol, allylurea 1-allyltheourea (thiosine-amine), vinyl-amine, vinyl-alcohol  
20 or allyl-amine.
- c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold  
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- d) optionally providing a metallization of the surface by using a conventional electroless bath, or
- avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization.  
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- Step b) may start before step a) provided that step b) does not terminate until step a) is started, simultaneously with step a), under step a), or follow immediately  
35 after step a). Step c) may start before step b), simulta-

neously with step b), follow immediately after step b) or within 8 months after step b), preferably within 6 months, and step d) may follow step c) or start simultaneously with step d).

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The method is preferably carried out in a reactor at least partly evacuated from air and water vapour. Further, the reactor should have a channel for feeding the working gas, and a channel for feeding the monomer or monomer mixture. The monomer or monomer mixture is introduced as a gas, e.g. by evaporation from a bottle.

Gas is fed into the reactor, and the plasma is generated (step a). Before, simultaneously or shortly thereafter monomer or monomer mixture is fed into the reactor (step b).

It is noted that the polymerisation preferably should be carried out at plasma discharge parameters resulting in a surface containing chemical groups promoting acid-base reactions with the subsequently deposited metal layer.

The generation step a) is preferably, as stated in claim 11, carried out for a period of between 0.01 and 1000 seconds, preferably between 1 and 500 seconds, more preferably between 10 and 60 seconds, and the treatment step b) is preferably carried out for a period of between 0.1 and 1000 seconds, preferably between 1 and 500 seconds, more preferably between 10 and 200 seconds.

The treatment step b) may continue when step a) has ended, even though there no longer are generated radicals on the substrate surface. This continuation of step b) will then result in a polymerisation of monomers onto the

new polymeric layer which already have been bound to the polymer surface.

If the surface of the polymer substrate is contaminated with water, oil or other contaminants, step a) is preferably carried out for more than 30 seconds, and step b) is started 10 to 30 seconds after step a) so as to clean the surface before the monomers are polymerised onto the substrate surface.

10           The partial pressure of the gas or the plasma in step a)  
is preferably between 0.1 and 10000 Pa.

The monomer pressure in step b) is preferably, as stated  
15 in claim 10, between 0.1 and 10000 Pa, more preferably  
between 10 and 1000 Pa.

The temperature is not important but should preferably, as stated in claim 14, be the same under both step a) and step b) and preferably the temperature under both step a) and step b) is between 250 and 450 K, most preferably between 280 and 330 K.

The total pressure, i.e. the sum of the partial pressures of the air, optionally water vapour, the gas or plasma and the monomer, under step a) is preferably, as stated in claim 15, equal to the total pressure under step b), the total pressure is preferably between 0.2 and 100000 Pa, more preferably between 0.2 and 10000 Pa, and most preferably between 10 and 1000 Pa.

The polymer substrate can be any polymer material provided that free radicals are created on the surface of the material when it is subjected to a gas plasma or  
35 other means of radical generation.

Preferably, as stated in claim 6, the polymer substrate is a polyolefine type, such as PE, PP, or an aryl type, such as styrene, a diene type, such as polybutadiene, polyisoprene, a silicone type, such as silicone rubber, a  
5 fluorine type, such as polytetrafluorethylene or its co-polymers.

The substrate can have any shape and any size, and may comprise complicated geometries. Preferably the polymer  
10 substrate is in the form of film, sheet, pipe, rod, porous or non-porous body, fabric, non-woven fabric, fibres or threads and/or as profiles made by extrusion, compression moulding, injection moulding, thermoforming or vacuum forming.

15 The generation of radicals on the substrate surface is preferably obtained by subjecting the substrate to a plasma discharge.

20 The plasma can be generated by any known methods, but preferably, as stated in claim 9, the gas plasma is generated by excitation of a gas in a direct current (DC), low frequency (LF), radio frequency (RF) or microwave (MW) generated electric field. Most preferably the gas  
25 plasma is generated by excitation of a gas in a direct current (DC) or by excitation using low frequency (LF).

The intensity of the used gas plasma should preferably have a level ensuring creation of radicals in the polymer  
30 surface. If the level is too high, this may result in severe damage of the bulk-polymer (depolymerisation). Hence, the power level of the plasma should be optimised so that surface radicals are created, but no serious damage is made to the bulk.

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A preferred method of generating a plasma discharge is described in the applicant's European patent application No. EP 96610018.2.

- 5 Preferred embodiments for the invention are specified in claims 2 - 15.

10 *Experimental systems*

Although it is possible to carry out all necessary steps in a single vacuum vessel, initial experiments were carried out in two separate systems. In one of the systems  
15 the virgin polymer surface was altered by the use of a plasma treatment using a working gas and monomers. In the other vacuum system metal atoms were subsequently deposited to the surface of the test samples. Although possible in an industrial production, the approach of using  
20 separate machines for the two steps is highly inefficient. The results obtained from these experiments do, however, reflect the results obtainable if a custom made system, able to perform both tasks is used.

25 The first step was on all samples carried out in an experimental plasma system, essentially consisting of a 22 litre vacuum vessel having two inlet channels for gas and for monomer, respectively, and an electrode arrangement as described above with reference to the applicant's EP  
30 application No. 96610018.2 The plasma is generated using the 3-phase technique described above with a frequency of 50 Hz and  $U_0$  of 240 to 280V. 27 electrodes are arranged in a circle around the vacuum vessel with a diameter of 17 cm. Every third of the electrodes is connected to  $U_r$ ,  
35 another every third of the electrodes is connected to  $U_s$ ,

and the last every third of the electrodes is connected to  $U_t$ .

The second step was on all samples carried out in an experimental plasma system, essentially consisting of a glass bowl having an internal volume of 15 litres. To atomise the metal and transfer it from the target to the sample surface a custom made magnetron was constructed. The magnetron is essentially a copper plate, having a diameter of 10 cm and a thickness of 4 mm. The back-side of the copper plate is shielded using a ceramic container. On the backside of the copper-plate a magnet is mounted. The magnetron is operated by applying a negative DC potential of 450 V. During operation a current of 0.05 A is drawn between the magnetron and the positive parts of the chamber. During all experiments argon is used as the working gas for the magnetron.

Both plasma systems are pumped using the same vacuum system comprising an Edwards EH 250 Roots-blower, backed by an Alcatel rotary vane pump. The pressure is monitored using an Alcatel pirani-gauge, mounted on the start of the pumping-line.

During step a) and b) the sample is held at floating potential.

#### Example 1

Covering a 100x50x3 mm sheet of polytetrafluorethylene (PTFE) with a conductive layer of metal.

#### Step 1

The sheet was subjected to an argon plasma discharge, generated as described above, for 20 s at a pressure of

0.1 mbar. Hereafter a vapour essentially comprising of 2-ethyl cyano acrylate and glycidylmetacrylate was let into the argon plasma at a pressure of 0.15 mbar for 30 s.

5    Step 2

After this treatment 100 nm of silver (Ag) was deposited onto the surface, making the surface conductive. The deposition was accomplished by using a silver sheet as a target on the magnetron, and the magnetron was operated  
10    for 60 seconds.

Step 3

After Ag deposition, the sheet was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in step 1 and 2  
15    an adherent copper coating was formed where Ag was deposited.

The copper layer can be 0.5  $\mu\text{m}$  or more, depending on the  
20    treatment time in the electroless copper bath. The average thickness obtained after a given time is as claimed by Shipley 2.5  $\mu\text{m}$  per hours.

The adhesion strength of the copper layer was examined by  
25    the standard well known to people skilled in the art, DIN 53 151 having a scale from GT 0 to GT 5, where zero is excellent. The treated sample in this example complied the standard and got the score Gt 0 - Gt 1.

30    Example 2

Covering of a component made from polypropylene (PP) with a shielding metallic layer.

## Step 1

The component was subjected to an argon plasma as described above for 10 s at a pressure of 1 mbar. Hereafter a vapour essentially comprising of toluene-2,4-diisocyanate was let into the plasma chamber at a pressure of 2 mbar for 20 s.

## Step 2

After this treatment 2 ML (monolayers) of platinum (Pt) was accomplished by using a Pt sheet as a target on the magnetron, and the magnetron was operated for 5 seconds.

## Step 3

The component was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in steps 1 and 2 an adherent copper coating was formed where Pt was deposited on the PP component.

20 Example 3

Covering a PTFE surface with a 0.5  $\mu\text{m}$  metal layer.

Steps 1 and 2 were conducted as described in example 2.

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## Step 3

The component was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in steps 1 and 2 an adherent copper coating was formed where Ag was deposited.

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Example 4a

35 Covering a PTFE surface with a 5  $\mu\text{m}$  metal layer.

Steps 1 - 2 identical to the steps in example 2.

### Step 3

Copper was then deposited on the Ag covered surface using  
5 a conventional electroplating technique.

Example 4b

Covering a PTFE surface with a 5  $\mu\text{m}$  metal layer

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Steps 1 - 3 identical to the steps in example 3

### Step 4

More copper was then deposited on the surface using a  
15 conventional electroplating technique.

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